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A METHOD FOR FIELD CALIBRATION  
OF THE PA260 PHOSPHORUS ANALYZER  
USING SOLID ADSORBENT MATERIALS

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December 1989



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## PREFACE

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# A METHOD FOR FIELD CALIBRATION OF THE PA260 PHOSPHORUS ANALYZER USING SOLID ADSORBENT MATERIALS

## 1. INTRODUCTION

In recent years, monitoring plant personnel for trace exposures to chemicals has become a huge priority for both industry and government installations. The objectives of this study were to find a suitable means for rapid field calibration of the PA260 phosphorus analyzer and to develop the capability of using solid adsorbents to detect personnel exposure levels to chemicals in a plant environment. The solid adsorbent approach has two major advantages over other traditional air sampling devices such as bubblers or impingers. The sampling time and rate of sampling is dramatically reduced; and the time required to collect a sample on a solid adsorbent has been shown to be 60 times faster than using a bubbler.\* The size of the solid adsorbent and ease of analysis makes multiple sampling practical and efficient.

This report covers a method for collecting triethyl phosphate (TEPO) on two types of solid adsorbent materials, TENAX-GC and Chromosorb 106. The TEPO was detected, and concentrations were verified on the Columbia Scientific Industries Corporation (Austin, TX) PA260 Phosphorus Analyzer and by bubbler technology. This study can serve as the basis for the reliability of the solid adsorbent approach to multiple sample analysis. In addition, field calibration of PA260 detectors and subsequent solid adsorbent confirmation feasibility has been demonstrated. (AJD)

## 2. SOLID ADSORBENT EXPERIMENTATION

### 2.1 Equipment and Materials.

Triethyl phosphate, 99+%, was used in this study. The analysis was conducted using the Perkin-Elmer Corporation (Rockville, MD) 8500 Gas Chromatograph (GC) linked to the Perkin-Elmer Automatic Thermal Desorption System, Model 50 (ATD-50). The GC was equipped with a 15 m by 0.54 mm i.d. delta bonded 5 (methyl-phenyl polysiloxane) liquid phase column. Film thickness for this column is 1  $\mu$ m.

Solid adsorbent tubes were hand packed with TENAX-GC (60/80 mesh) or Chromosorb 106 (80/100 mesh). Both adsorbents were supplied by Alltech Associates (Deerfield, IL). The adsorbents were packed in stainless steel tubes supplied by Perkin Elmer. The TEPO obtained from Aldrich Chemical Company, Incorporated (Milwaukee, WI) was used as received. Propylene glycol was obtained from the Fisher Scientific Company (Silver Spring, MD). Trimethyl pentane was used to trap the TEPO vapor standards. Standard TEPO concentrations were prepared in ranges from 0.8 to 7  $\mu$ m/mL. The injection and trap calibration of samples were performed using various sizes of microliter syringes.

\*ETTzy, M., Ferguson, F., Janes, L., and Paterno, D., Solid Adsorbent Trace Analysis of DMMP and TEPO, CRDEC-TR-027, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, January 1989, UNCLASSIFIED Report.

## 2.2 Generation of TEPO Vapor Concentrations.

Vapor standards of TEPO were generated using a portable gas generator developed by the U.S. Government in the early 1960s. The TEPO concentrations were generated for the solid adsorbent tubes and bubblers using a 5% solution of TEPO in propylene glycol. Ten milliliters of solution were placed in an Edgewood Arsenal 25-mL bubbler (impinger) that was then connected in the portable gas generator. Figure 1 illustrates a block diagram of the pneumatics of the gas generator. A pump produced a flow of air, which was divided into two air streams by a Y connector. Both streams were directed to and controlled by rotometers, one for the source and the other for dilution. One air stream flowed from the source rotometer and bubbled through the TEPO solution, producing TEPO vapor. The second stream from the dilution rotometer was rejoined with the source flow and diluted the TEPO vapor stream. The final diluted TEPO stream was directed to a mixing chamber and finally to a three-port sampling manifold, where the solid adsorbent tubes or the PA260 analyzer sampled the gas stream.

To verify the TEPO concentrations produced by the gas bubbler, the streams of air containing the various TEPO concentrations were bubbled through trimethyl pentane. The TEPO dissolved in the trimethyl pentane and was subsequently analyzed using GC as described in Section 2.4.5.

## 2.3 Sample Standards.

Five calibration points were generated from 0.875 to 7.0  $\mu\text{g/mL}$  of TEPO in trimethyl pentane. A 5% solution of TEPO in propylene glycol was prepared, and 10 ml was transferred to an Edgewood Arsenal vapor bubbler for the preparation of TEPO vapor standards.

## 2.4 Procedures.

### 2.4.1 Calibration Curve.

Once the GC and ATD-50 conditions were established, a calibration curve was generated. Duplicate injections of TEPO at concentrations ranging from 0.875 to 7.0  $\mu\text{g/mL}$  were made directly into the heated injection port of the ATD-50. After volatilization, the sample was swept into the cold trap where it was concentrated. After concentration, the cold trap carrier flow was reversed. The cold trap was ballistically heated (25-250°C in 30 s), vaporizing the concentrated TEPO plug and sweeping the material onto the column for separation and then detection by the flame photometric detector (FPD). The ATD-50 parameters for the calibration curve were as follows:

|                                   |        |
|-----------------------------------|--------|
| Delay between start and injection | 2 min  |
| Oven temperature                  | 250 °C |
| Desorption time                   | 5 min  |
| Box temperature                   | 150 °C |
| Cold trap low temperature         | 25 °C  |
| Cold trap high temperature        | 250 °C |
| Analysis time                     | 5 min  |
| Cycle time                        | 18 min |

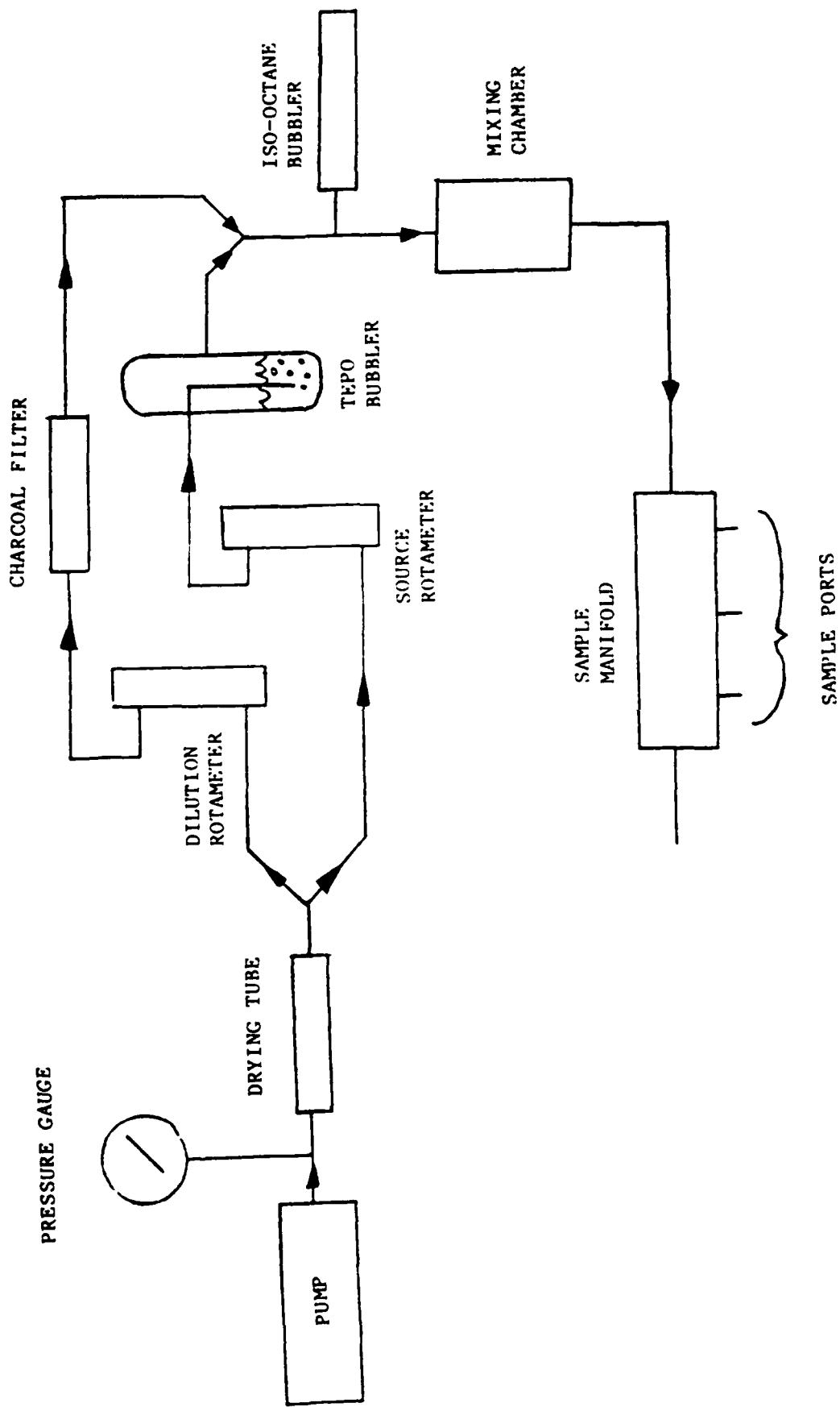


Figure 1. Pneumatic Network of Portable Gas Generator

The delay between start and injection was a time period established to allow an adequate, uniform collection of vaporized TEPO onto the cold trap before cold trap desorption was initiated.

NOTE. This process is actually a single-stage desorption method.

#### 2.4.2 Gas Generator Sampling.

Sampling of the gas standards generator involved a solid adsorption and a desorption procedure. The generator was challenged with 10 tubes containing TENAX-GC and 10 tubes containing Chromosorb 106. Each tube challenged the generator for 5 min with predried air at a flow rate of 100 cm<sup>3</sup>/min. The ATD-50 parameters for the two-stage desorption were as follows:

|                            |        |
|----------------------------|--------|
| Oven temperature           | 250 °C |
| Desorption time            | 15 min |
| Box temperature            | 150 °C |
| Cold trap low temperature  | 25 °C  |
| Cold trap high temperature | 250 °C |
| Analysis time              | 20 min |
| Cycle time                 | 37 min |

#### 2.4.3 Solid Adsorbent Analysis.

Once loaded into the automated 50-sample rack of the ATD-50, the solid adsorbent tubes were processed using the two-stage desorption system. The solid adsorbent tube was pressure checked before loading into the heated oven (box) of the ATD-50. After successfully passing a pressure check, the heated tube was swept with carrier gas, and the vaporized sample was collected onto the cold trap. The cold trap was then ballistically heated (25-250 °C in 30 s), and the carrier flow path was reversed to concentrate the sample in a thin band that was then swept from the cold trap through the fused silica transfer line to the column for chromatography.

NOTE: The preceding GC parameters were used throughout the study.

#### 2.4.4 Chromatography of Desorbed Material.

The GC was a Perkin-Elmer Model 8500. The gas chromatographic parameters established for chromatographing the desorbed TEPO were as follows:

|  |                           |       |
|--|---------------------------|-------|
| Column   | DB-5 15 m by 0.54 mm i.d. |       |
| Liquid phase                                   | 1-μm film thickness       |       |
| Stages   | Initial                   | Final |
| Oven temperature (°C)                          | 90                        | 250   |
| Time (min)                                     | 2.5                       | 15.0  |
| Ramp Rate (°C/min)                             | 30.0                      |       |
| FPD 1 response: fast                           |                           |       |
| FID 2 sensitivity: low                         |                           |       |
| Detector zero (autozero)                       |                           |       |
| Initial detector 1 (detector currently in use) |                           |       |
| Injector 1 temperature: 200                    |                           |       |
| Injector 2 temperature: off                    |                           |       |

Detector 1 temperature: 300  
Detector 2 temperature: 250  
Flow 1: 10 mL/min  
Flow 2: 2 mL/min  
Carrier gas 1: helium  
Carrier gas 2: N<sub>2</sub>  
Equilibrium time: 0.1 min  
Total run time: 22.8 min

The preceding parameters were used for all TEPO analyses, including calibration runs and bubbler analyses.

The sampling and analysis process was repeated for four concentrations. Each concentration was challenged three times. After completion of a solid adsorbent challenge, an impinger type bubbler containing 10-cm<sup>3</sup> of trimethyl pentane maintained at -78 °C was used to confirm the concentrations of the gas standard collected by solid adsorbent.

#### 2.4.5 TEPO Buttler Analysis.

Buttlers were analyzed using the preceding GC parameters. Sample introduction was the same as that described in Section 2.3.4. The injected volumes were 1  $\mu$ L per analysis. Each bubbler was analyzed on two GCs to ensure accuracy of concentrations collected. Concentration values were determined by the external standard response factor approach. These values were then compared to the values obtained using the solid adsorbent technique. This procedure provided a check on the reliability of the solid adsorbent, bubbler, and gas-generation source.

#### 2.4.6 Solid Adsorbent Sampling Method Modifications and Results.

Due to the low response of the FPD, it was necessary to increase the flow that sweeps the adsorbed TEPO from the cold trap to the detector. The flow was increased to 30 mL/min, a 20 mL/min increase over the initial value reported. To shorten the overall analysis time, 3 instead of 10 tubes were used for each solid adsorbent packing. Investigators established that the statistical error for 10 tubes was no better or worse than that for 3 tubes once the TEPO generator had stabilized. It was determined by the PA260 that the portable generator required a 20-min equilibration time to obtain stable concentrations initially and when flow rates were changed. The pump-generated air source of the portable generator was replaced with zero air because frosting and eventual stoppage resulted at the -78 °C cooling temperature necessary for the trimethyl pentane collection media. Subsequent follow-up solid adsorbent data was collected using bone dry air in place of the pumping air source. The nonpumping air source provided high purity air (99.97%) that connected to the portable generator in the same fashion as the pump.

### 3. PA260 PHOSPHORUS ANALYZER EXPERIMENTATION

#### 3.1 Description of the PA260.

The PA260 phosphorus analyzer, manufactured by Columbia Scientific Industries, performs real-time analysis of phosphorus compounds in gas mixtures.

The analyzer uses a FPD assembly and optics system that is specifically for measuring phosphorus-containing compounds. This self-contained unit consists of four basic subsystems: the pneumatic subsystem; the FPD burner block assembly; a photomultiplier tube (PMT) assembly; and electronics for controlling operating parameters and signal conditioning. Figure 2 illustrates the pneumatic network of the PA260.

Sample gas is drawn by a vacuum pump through an inlet port on the back of the instrument and is delivered directly to the FPD burner assembly. Hydrogen is introduced at 40-60 psi to the burner assembly through a temperature-controlled capillary and rotometer. This method of hydrogen introduction and careful maintenance of the burner block temperature (150 °C) produces a stable flame in environments of larger temperature fluctuations. The sample gas and hydrogen are mixed in the burner block and sent to the burner tip where the sample undergoes combustion. The burned sample emits bands of visible light whose emission intensity is detected by the PMT. The use of a narrow band pass filter (526 nm) selectively passes the emission to measure only phosphorus-containing compounds. The current output of the PMT is converted to a voltage by an amplifier board and may be measured at output jacks located on the back of the analyzer.

There are two methods of measuring current output from the PA260. Both methods yield linear log-log calibration plots. By using the "range" settings on the front of the instrument, the user may select a 0-1 v or 0-100 mV full-scale output for the range selected. There are six ranges currently available:  $10^{-9}$ ,  $10^{-8}$ ,  $10^{-7}$ ,  $10^{-6}$ ,  $10^{-5}$ , and  $10^{-4}$  amps full scale. In addition, the current output may be measured using the "log" setting. This mode of operation provides 0-1 v (or 0-100 mV) full-scale output for the entire six decades of input current. Figure 3 illustrates the conversion of chart readings to current while using this mode.

### 3.2 Sampling Method Using the PA260.

Concentrations of TEPO were sampled by the PA260 through a 2-m length, 1/8 in. o.d. Teflon tubing at a factory-set flow rate of 240 mL/min. After zeroing the analyzer, the PA260 was challenged for a minimum of 10 min per exposure; this challenge was followed by exposing the analyzer to zero air until the original baseline was obtained.

Data were recorded on an Ohmega Engineering, Incorporated (Stamford, CT) Model 585 Strip Chart Recorder and a Hewlett-Packard (Rockville, MD) Model 3466 Digital Voltmeter. A 1-s time constant was used throughout this study.

## 4. RESULTS

### 4.1 Solid Adsorbent Tubes.

The data was collected using both solid adsorbent materials using a 5% TEPO solution in the portable gas generator. Both adsorbents were also able to collect measurable concentrations using a 1% TEPO solution, but data were not reproducible due, in part, to the inability of the portable gas generator to deliver stable, reproducible TEPO concentrations at levels below 0.05 parts per billion (ppb). These concentrations are below the PA260's detection limit.

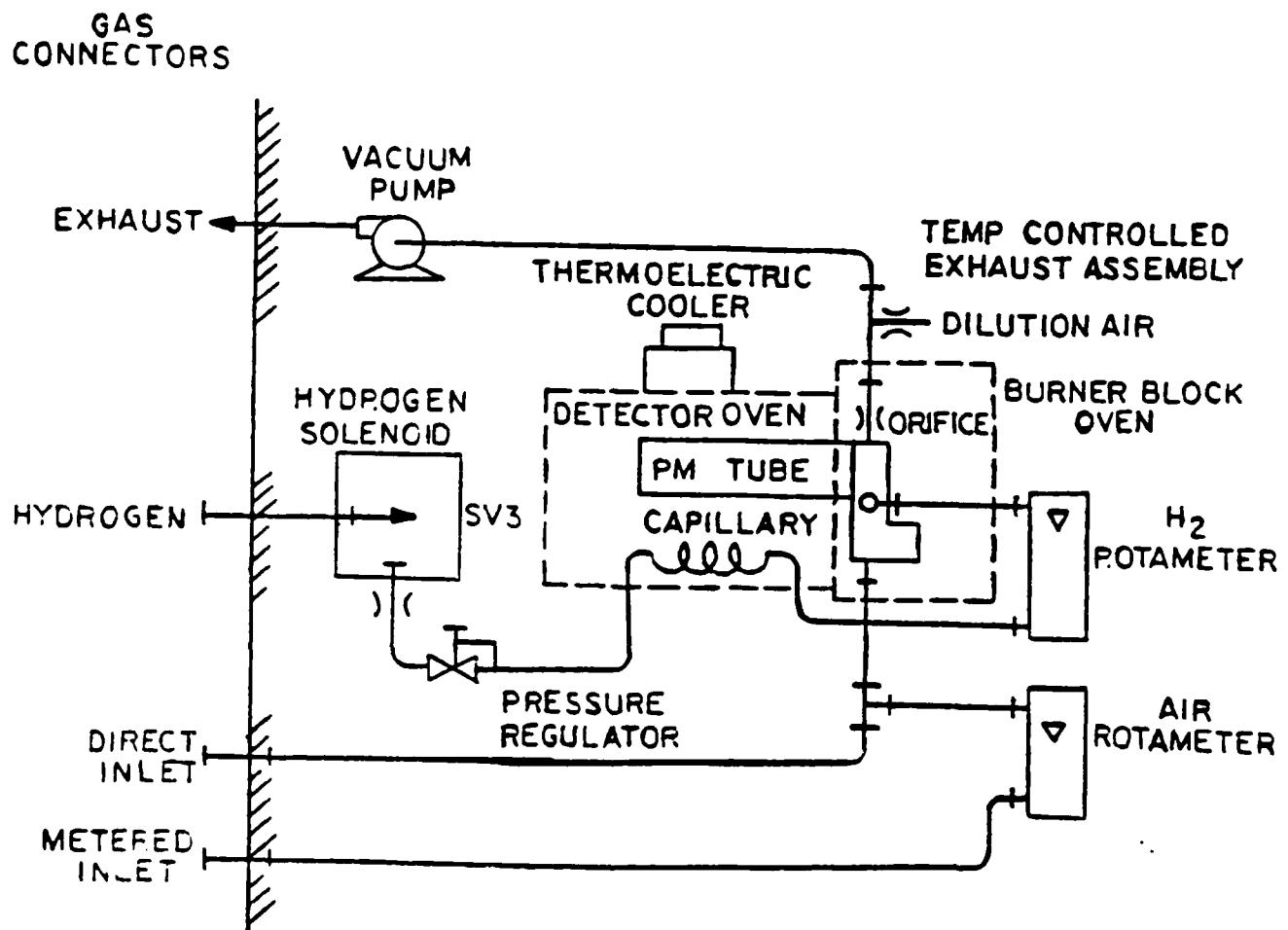
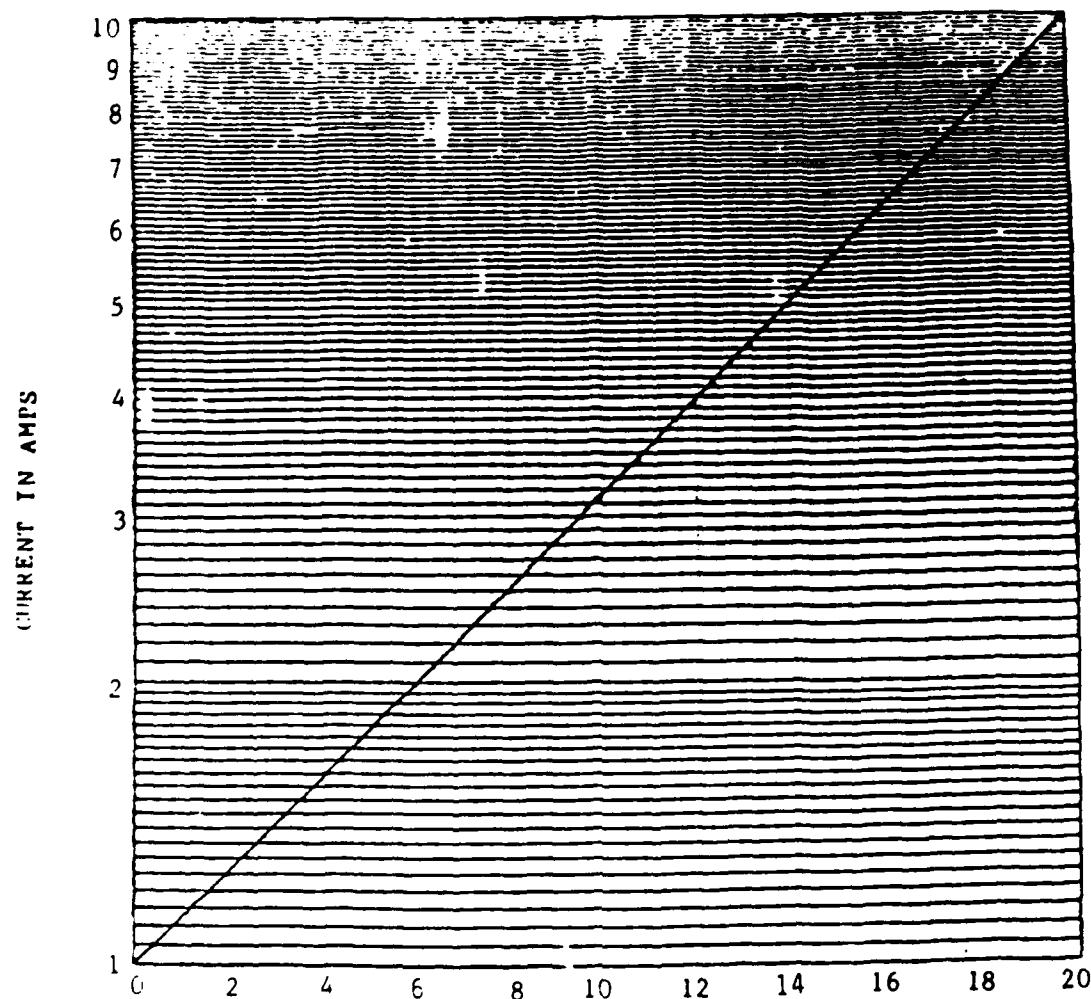


Figure 2. Pneumatic Network of PA260



PERCENT OF FULL SCALE ABOVE (0%, 20%, 40%, 60%, 80%)

RECORDER READING

0%  
20%  
40%  
60%  
80%  
100%

CURRENT IN AMPS

$1 \times 10^{-9}$   
 $1 \times 10^{-8}$   
 $1 \times 10^{-7}$   
 $1 \times 10^{-6}$   
 $1 \times 10^{-5}$   
 $1 \times 10^{-4}$

Figure 3. Recorder Output for Log Scale

With a 5% TEPO solution, both TENAX-GC and Chromosorb 106 were able to reproducibly adsorb TEPO concentrations of 0.0022 mg/m<sup>3</sup> (0.29 ppb). Both adsorbents have positive and negative characteristics for this application. For example, TENAX-GC has a relatively higher collection efficiency than Chromosorb 106 especially at very low concentration, and TENAX-GC is less sensitive to humidity than Chromosorb 106. This could be due to the higher surface area of the TENAX-GC. The data collected on Chromosorb 106 is somewhat more reproducible at lower concentrations. It is evident that the end user of the solid adsorbent materials must examine all environmental conditions and the desired accuracy when choosing a material. Table 1 contains Chromosorb 106 and accompanying bubbler data. Experimental error between the average part per billion values obtained for solid adsorbent versus bubbler are 2%, 3%, 9%, and 8%, respectively, for each of the gas generator rotometer flow settings. Concentration detected and airborne concentration collected all have approximately a 10% error between data points. When analyzing data on the solid adsorbent half of Table 1, the bubbler half of that table exhibits approximately the same 10% error. These percentage errors in measurement indicate a 70-ppb deviation in the solid adsorbent's ability to trap TEPO versus that of the bubbler method at concentrations less than 0.3 ppb. Factors contributing to this deviation are packing material chosen, length of sampling time at this level (10 min versus 12 hr), and finally the inability of the generator to produce a stable concentration at the 0.3-ppb level.

The TEPO concentrations obtained from the solid adsorbent tubes were verified using a bubbler containing trimethyl pentane. Table 2 shows the TEPO concentrations obtained from the solid adsorbent tubes compared to concentrations obtained from the trimethyl pentane bubblers. The table also shows the response of the PA260 at these concentrations. The PA260 analyzer operation and data from these TEPO concentrations are discussed in detail in Section 4.2. As illustrated, excellent data correlation is obtained between concentrations obtained from solid adsorbent tubes and bubblers, indicating that the solid adsorbed method of sampling airborne TEPO concentrations is both accurate and reproducible.

#### 4.2 PA260 Phosphorus Analyzer.

##### 4.2.1 Baseline Stability of the PA260.

The baseline stability of the PA260 was evaluated to determine any drift of the analyzer over time. Sample gas was drawn through a charcoal filter canister supplied with the instrument to provide zero air to the analyzer. The instrument was allowed to run continuously for 60 hr under ambient laboratory conditions in the log/normal mode. Tables 3, 4, and 5 show analyzer response over time. No significant baseline drift was observed over the entire test period. Overall standard deviation drifts were determined to be <0.5% over any 24-hr period and <0.6% over any 60-hr period.

##### 4.2.2 Calibration Curve for TEPO.

Calibration curves were obtained for TEPO on the PA260 analyzer using both the range settings and the log/normal mode of operation. The resulting data using the 10<sup>-8</sup>- and 10<sup>-7</sup>-amp ranges is summarized in Table 6. The first

Table 1. Collection/Recovery from 5% TEPO Solution

| Solid Adsorbent Tubes              |                                     |                  | Bubblers                       |                                     |                  |
|------------------------------------|-------------------------------------|------------------|--------------------------------|-------------------------------------|------------------|
| Conc<br>Detected<br>( $\mu$ g)     | Collected<br>Airborne<br>Conc (ppb) | Average<br>(ppb) | Conc<br>Detected<br>( $\mu$ g) | Collected<br>Airborne<br>Conc (ppb) | Average<br>(ppb) |
| <u>Dilution Air 120, Agent 17:</u> |                                     |                  |                                |                                     |                  |
| 1.6288                             | 0.218                               |                  | 2.0967                         | 0.396                               |                  |
| 2.0795                             | 0.287                               | 0.291            | 1.6272                         | 0.314                               | 0.364            |
| 2.7426                             | 0.368                               |                  | 1.9977                         | 0.382                               |                  |
| <u>Dilution Air 120, Agent 35:</u> |                                     |                  |                                |                                     |                  |
| 2.8129                             | 0.382                               |                  | 1.0740                         | 0.409                               |                  |
| 3.3136                             | 0.450                               | 0.427            | 1.454                          | 0.437                               | 0.414            |
| 3.2614                             | 0.450                               |                  | 1.0560                         | 0.396                               |                  |
| <u>Dilution Air 120, Agent 70:</u> |                                     |                  |                                |                                     |                  |
| 5.7121                             | 1.56                                |                  | 5.6046                         | 2.13                                |                  |
| 7.2362                             | 1.98                                | 1.89             | 5.3699                         | 2.03                                | 2.07             |
| 7.7441                             | 2.12                                |                  |                                |                                     |                  |
| <u>Dilution Air 60, Agent 70:</u>  |                                     |                  |                                |                                     |                  |
| 10.4556                            | 2.85                                |                  | 6.3033                         | 3.59                                |                  |
| 12.3989                            | 3.38                                | 3.25             | 6.0921                         | 3.47                                | 3.52             |
| 12.8531                            | 3.51                                |                  | 6.1705                         | 3.51                                |                  |

Table 2. Comparison of TEPO Concentrations (ppb): Solid Adsorbent Tubes Versus Trimethyl Pentane Bubblers

| PA260 Phosphorus* |         |                             |
|-------------------|---------|-----------------------------|
| Tubes             | Bubbler | Analyzer Response<br>(amps) |
| 0.291             | 0.364   | $4.1 \times 10^{-10}$       |
| 0.427             | 0.414   | $8.1 \times 10^{-10}$       |
| 1.89              | 2.07    | $2.22 \times 10^{-9}$       |
| 3.25              | 3.52    | $5.50 \times 10^{-9}$       |

\*Current readings obtained using individual range settings.

Table 3. Baseline Stability of the PA260 Phosphorus Analyzer - Day 1.

| No. of Test | Amps<br>( $\times 10^{-8}$ ) | Time<br>(hr) |
|-------------|------------------------------|--------------|
| 1           | 1.30                         | 1            |
| 2           | 1.34                         |              |
| 3           | 1.34                         |              |
| 4           | 1.30                         |              |
| 5           | 1.30                         |              |
| 6           | 1.30                         |              |
| 7           | 1.30                         |              |
| 8           | 1.30                         | 8            |
| 9           | 1.30                         |              |
| 10          | 1.28                         |              |
| 11          | 1.28                         |              |
| 12          | 1.28                         |              |
| 13          | 1.25                         |              |
| 14          | 1.28                         |              |
| 15          | 1.28                         |              |
| 16          | 1.28                         | 16           |
| 17          | 1.30                         |              |
| 18          | 1.30                         |              |
| 19          | 1.34                         |              |
| 20          | 1.34                         |              |
| 21          | 1.37                         |              |
| 22          | 1.37                         |              |
| 23          | 1.37                         |              |
| 24          | 1.34                         | 24           |

$$\bar{x} = 1.30 \times 10^{-8}; \text{ SD} = 0.0011; \% \text{ SD} = 0.51$$

Table 4. Baseline Stability of the PA260 Phosphorus Analyzer - Day 2.

| No. of Test | Amps<br>( $\times 10^{-8}$ ) | Time<br>(hr) |
|-------------|------------------------------|--------------|
| 1           | 1.34                         | 25           |
| 2           | 1.30                         |              |
| 3           | 1.30                         |              |
| 4           | 1.30                         |              |
| 5           | 1.28                         |              |
| 6           | 1.28                         |              |
| 7           | 1.28                         |              |
| 8           | 1.28                         |              |
| 9           | 1.30                         |              |
| 10          | 1.25                         |              |
| 11          | 1.25                         |              |
| 12          | 1.25                         | 36           |
| 13          | 1.25                         |              |
| 14          | 1.28                         |              |
| 15          | 1.30                         |              |
| 16          | 1.30                         |              |
| 17          | 1.28                         |              |
| 18          | 1.25                         |              |
| 19          | 1.28                         |              |
| 20          | 1.28                         |              |
| 21          | 1.28                         |              |
| 22          | 1.28                         |              |
| 23          | 1.28                         |              |
| 24          | 1.25                         | 48           |

$$\bar{x} = 1.28 \times 10^{-8}; \text{ SD} = 0.001; \% \text{ SD} = 0.41$$

Table 5. Baseline Stability of the PA260 Phosphorus Analyzer - Day 3

| No. of Test | Amps<br>(x 10 <sup>-8</sup> ) | Time<br>(hr) |
|-------------|-------------------------------|--------------|
| 1           | 1.25                          | 49           |
| 2           | 1.25                          |              |
| 3           | 1.28                          |              |
| 4           | 1.25                          |              |
| 5           | 1.25                          |              |
| 6           | 1.25                          |              |
| 7           | 1.21                          |              |
| 8           | 1.21                          |              |
| 9           | 1.25                          |              |
| 10          | 1.21                          |              |
| 11          | 1.21                          |              |
| 12          | 1.21                          | 60           |

$$\bar{x} = 1.25 \times 10^{-8}; \text{ SD} = 0.001; \% \text{ SD} = 0.31$$

four concentrations illustrated in the table were obtained from a 5% TEPO solution collected on the Chromosorb 106 solid adsorbent tubes described earlier. The last data point was produced with a 30% TEPO bubbler solution and was calculated based on the 5% TEPO data. Relative percent standard deviations of approximately 2% were observed for each TEPO concentration except 0.0022 mg/m<sup>3</sup>. The large standard deviation observed for this data point can be attributed, in part, to the portable gas generator. This concentration was generated at a very low source flow rate where it is most difficult to obtain accurate and reproducible TEPO concentrations. In addition, a concentration of 0.0022 mg/m<sup>3</sup> (0.29 ppb) is actually below the detection limit of the PA260 (0.5 ppb or better) as established by the manufacturer.

The low concentration of TEPO produces a reproducible signal from the analyzer of 0.041 on the 10<sup>-8</sup>-amp scale. This represents 0.041 v by 10<sup>-8</sup> amps or 4.1 by 10<sup>-10</sup> amps. This concentration (0.0022 mg/m<sup>3</sup>) was determined to be the minimum detection limit (MDL) for TEPO using the PA260.

The data in Table 6 was used to generate the calibration plot (Figure 4) of net current versus TEPO concentration. This log-log plot exhibits good linearity (correlation 0.998115) and verifies the TEPO concentrations obtained using the Chromosorb 106 or TENAX-GC solid adsorbent tubes that can be read accurately by the PA260. The analyzer also showed good sensitivity, reliability, and reproducibility using the individual range settings.

Calibration data was also obtained for TEPO using the analyzer in the log/normal mode. The data is tabulated in Table 7. As described earlier, net currents were obtained from challenge voltages using Figure 3. We have observed poor correlation between calibration points obtained using the individual range settings as compared to the log/normal mode, especially below 0.0032 mg/m<sup>3</sup>.

We are currently investigating this problem using another PA260 analyzer to determine if the phenomenon occurs in this particular instrument or is due to a lack of linearity in the Columbia Scientific Industries Corporation circuitry when using low concentrations. Therefore, the use of the individual range settings is recommended for measuring concentrations below 1 ppb.

#### 4.2.3 Field Calibration of the PA260.

Calibration of PA260 analyzers in a field environment can be accomplished using the following: portable generator described in this report; several solid adsorbent tubes packed with the appropriate adsorbent; and a portable pump that can create and maintain a constant vacuum flow of at least 500 mL/min.

The PA260 operator sets up the portable generator and powers the unit. The flow rates for the rotometers that provide a concentration range for calibration are selected. Once this is completed and both the PA260 and portable generator have been stabilized, challenge of the generator is started. Beginning with the lowest value, the generator is challenged with the PA260 until a constant current value is obtained. This establishes the stability of the PA260 for that concentration and the generator source. When the PA260 and

Table 6. TEPO Calibration Data - Range Settings

| Date     | No. of Challenges | Avg. Challenge Voltage | Conc (mg/m <sup>3</sup> ) | % SD  | Scale              | Net Current (amps)    |
|----------|-------------------|------------------------|---------------------------|-------|--------------------|-----------------------|
| 2 May 88 | 14                | 0.041                  | 0.0022                    | 19.50 | 1x10 <sup>-8</sup> | 4.1x10 <sup>-10</sup> |
| 2 May 88 | 8                 | 0.081                  | 0.0032                    | 1.67  | 1x10 <sup>-8</sup> | 8.1x10 <sup>-10</sup> |
| 5 May 88 | 8                 | 0.222                  | 0.0141                    | 2.05  | 1x10 <sup>-8</sup> | 2.22x10 <sup>-9</sup> |
| 2 May 88 | 3                 | 0.055                  | 0.0242                    | 1.82  | 1x10 <sup>-7</sup> | 5.50x10 <sup>-9</sup> |
| 9 May 88 | 4                 | 0.174                  | 0.0845                    | 2.30  | 1x10 <sup>-7</sup> | 1.74x10 <sup>-8</sup> |

r = 0.998115 (correlation coefficient)

m = 2.07 x 10<sup>-7</sup> (slope)

b = -3.80 x 10<sup>-11</sup> (intercept)

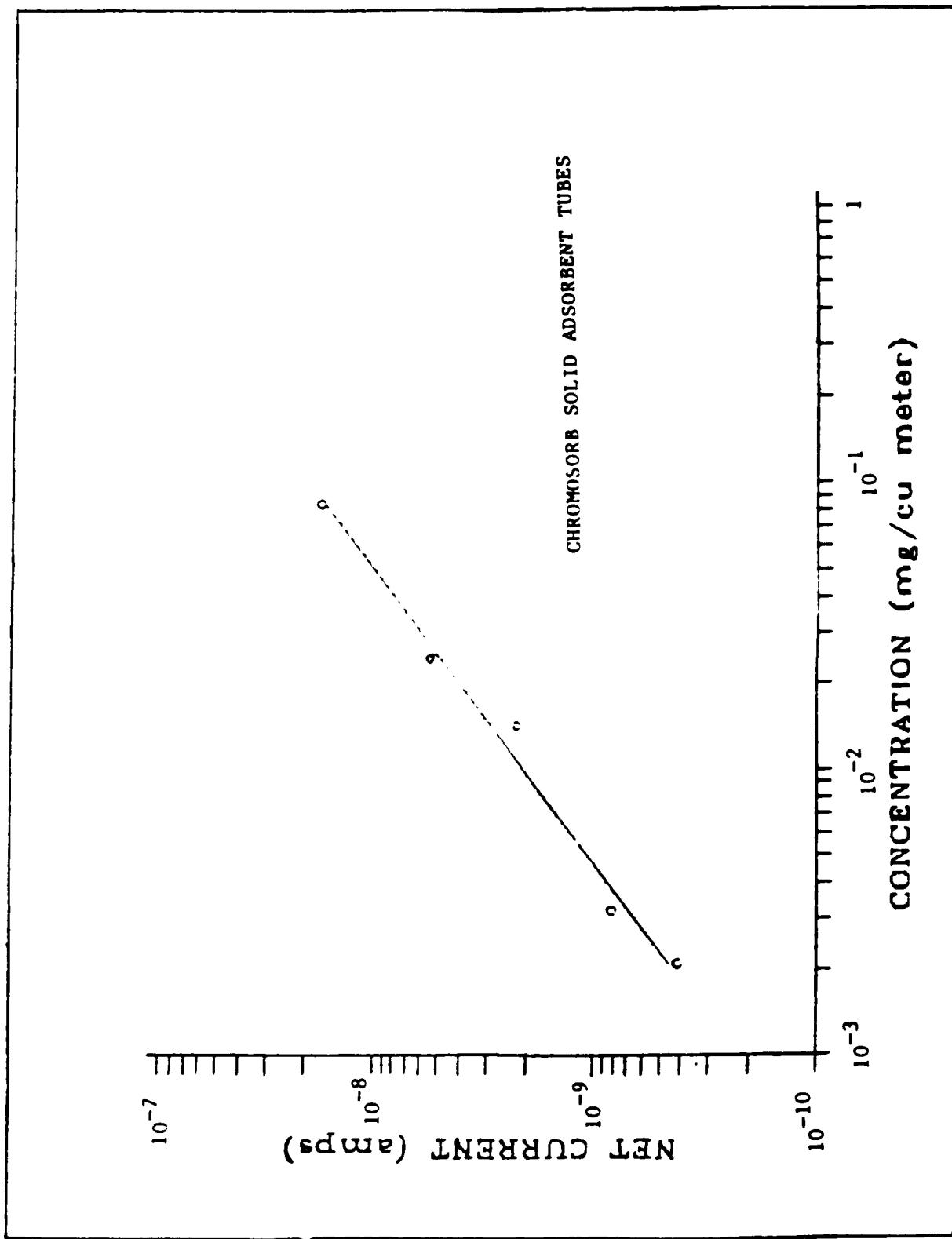


Figure 4. Calibration Curve for TEPO

Table 7. TEPO Calibration Data - Log/Normal

| Date      | No. of Challenges | Avg. Challenge Voltage | Conc (mg/m <sup>3</sup> ) | % SD | Net Current (amps)    |
|-----------|-------------------|------------------------|---------------------------|------|-----------------------|
| 16 May 88 | 8                 | 0.038                  | 0.0022                    | 5.70 | $1.5 \times 10^{-9}$  |
| 16 May 88 | 8                 | 0.055                  | 0.0032                    | 2.37 | $1.85 \times 10^{-9}$ |
| 12 May 88 | 8                 | 0.091                  | 0.0141                    | 1.10 | $2.81 \times 10^{-9}$ |
| 11 May 88 | 7                 | 0.168                  | 0.0242                    | 4.00 | $7.10 \times 10^{-9}$ |
| 13 May 88 | 4                 | 0.261                  | 0.0845                    | 2.62 | $2.03 \times 10^{-8}$ |

generating source are stabilized, solid adsorbent challenges follow. Two to three solid adsorbents challenged for 5 min per tube should result in reliable data.

The above process is repeated for the remaining two or more range points selected. The PA260 is now calibrated, and the calibration points can be verified when the solid adsorbent tubes are analyzed using a thermal desorption unit like that described in this study. Care must be taken to recap solid adsorbent tubes with storage caps until analysis has occurred.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The intended use of solid adsorbent for field calibrations and personal monitoring systems and/or sample collection devices is accurate and reproducible. The minimum detectable quantity can be extended if the sampling time is not a critical issue. One must keep in mind the minimum detectable quantity of the detection system when considering how long to sample the lowest concentration point. Our acceptable sampling time limit is 10 min. This time period allows the experimenter to complete a concentration curve in 3 hr or less, resulting in increased operator efficiency and more accurate data points.

Research into tube conditioning before use needs some attention. Our method allows 20 tubes to be conditioned. At one time, it was necessary to spend 1 week reprocessing the tubes through the ATD-50 despite strict adherence to the manufacturer's instructions concerning solid adsorbent conditioning. We recommend the tubes be conditioned 12-24 hr.

The effects of humidity on collection and desorption efficiency has not been determined. The humidity above 30% relative humidity compensated for in this study by cleaning up dilution air with a charcoal trap followed by drying the air with drierite.

The PA260 phosphorus analyzer as a real-time monitor has again been demonstrated to work effectively over a long period of time. As in previous studies, good correlation between data points and baseline stability of the unit when operated continuously has been demonstrated.

As a total field system, the PA260 analyzer in conjunction with the portable generator and solid adsorbents provides the analyst with the necessary tools to complete a field or plant environmental study without returning to the laboratory.